

## ARTEFACTS IN DETERMINING THE VAPOUR-PARTICULATE PHASE DISTRIBUTION OF ENVIRONMENTAL TOBACCO SMOKE NICOTINE

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### ABSTRACT

Nicotine in environmental tobacco smoke (ETS) resides predominantly in the aerosol vapour phase as a result of evaporation from the particles of sidestream smoke. In true ETS (*i.e.*, not concentrated or fresh sidestream smoke), the fraction of nicotine associated with the aerosol particulate phase is quite small, typically less than 5% of the total. Recently, some investigators have collected nicotine with sampling systems employing sorbent resin cartridges downstream from glass-fibre filters, and have attributed the nicotine retained on the glass-fibre filters to the particulate phase. The data reported here demonstrate that phase distributions and dynamics determined using glass-fibre filters are due to sampling system artefacts. Glass-fibre filters collect virtually all nicotine (vapour- and particulate-phase) at relatively short sampling intervals (1-2 min). The percentage of total nicotine trapped on the filter decreases with increasing sampling time. Using such a system, only that amount of total nicotine which exceeds the adsorptive capacity of the filter will break through and be collected by the sorbent medium. Attributing ETS particulate-phase nicotine to the quantity collected on a glass-fibre filter leads to erroneous conclusions regarding vapour-particulate phase dynamics.

Keywords: Aerosol, environmental tobacco smoke (ETS), nicotine, particles, vapour

### INTRODUCTION

It is now firmly established that nicotine in environmental tobacco smoke (ETS) resides predominantly in the aerosol vapour phase as a result of evaporation from the particles of sidestream smoke. This finding was first presented in 1985 (1), published the following year (2), and verified by other researchers (3). During these investigations, numerous independent analytical techniques were used to reach this conclusion, including: denuder sampling (2,3) and denuder, filter and sorbent bed sampling in concert with electrostatic precipitation and real-time detection by atmospheric pressure chemical ionization (APCI) mass spectrometry (2).

The fraction of true ETS (*i.e.*, not concentrated or fresh sidestream smoke) nicotine associated with the aerosol particulate phase is quite small, typically less than 5% of the total (2-6). However, there are indications that

the vapour-particulate distribution of ETS nicotine can be perturbed by exaggerated smoke concentrations (4) and by intense UV irradiation of the smoke (6). For example, with test chamber nicotine concentrations of ca.  $100 \mu\text{g m}^{-3}$ , 99% of total nicotine is in the gas phase while at chamber concentrations of ca.  $500 \mu\text{g m}^{-3}$ , 92% of the total is gas-phase nicotine (4). It is not known to what extent, if any, these perturbations may affect nicotine measurements in typical, real-world environments; however, ETS nicotine concentrations above  $100 \mu\text{g m}^{-3}$  are rarely encountered (7). In addition, the absolute certainty of these percentages is debatable due to the dynamic nature of the ETS aerosol and due to the fact that nicotine is highly adsorptive and is a semivolatile compound which tends to evaporate readily from aerosol particles. As such, it is not easy to measure phase distribution precisely because it is easily disturbed by the method of measurement.

Recently, Neurath *et al.* (8,9) and Esquier

and Hée (10) reported concentrations and time variations in the particulate-phase distribution of ETS nicotine that are contrary to the established theory of dynamics. These investigators collected nicotine with sampling systems employing sorbent resin cartridges downstream from glass-fibre filters and attributed the nicotine retained on the glass-fibre filters to the particulate phase. The adsorption of nicotine on glass-fibre filters was examined in the investigation reported here and the findings explain the deviation in apparent nicotine phase residence obtained using glass-fibre filters. Consequently, recent results concerning phase dynamics derived from nicotine collected on glass-fibre filters (8-10) are in error.

Determining which phase of ETS aerosol contains nicotine is not merely an academic pursuit. The phase residence is important in studying ETS exposure in that it may impact the mechanism and magnitude of nicotine retention by non-smokers. Also, there are significant consequences for predicting decay mechanisms of nicotine in indoor spaces as well as in understanding the variability between nicotine and other components of ETS and, ultimately, in determining the usefulness of nicotine as an ETS marker.

## MATERIALS AND METHODS

### Environmental Chamber

Test atmospheres were generated in an 18-m<sup>3</sup> environmentally-controlled test chamber (11). The chamber was ventilated continuously at eight air changes per hour. Temperature and relative humidity (RH) of the chamber air were nominally 20°C and 58%, respectively. Actual temperatures fluctuated between 20 and 22°C due to the presence of one person throughout the experiments.

### Nicotine Vapour Generation

Nicotine vapour was generated using a model 585A Precision Gas Standards Generator (Kin-Tek Laboratories, Inc., Texas City, TX). Nicotine vapour was swept by dry (0% RH) nitrogen from a sealed, thermostated (100°C) glass reservoir containing a diffusion tube of nicotine liquid. The Teflon tubing carrying the nicotine vapour was routed into the test chamber where the gas stream was diluted with humidified chamber air to achieve target nicotine concentrations. The resulting humidity of the

mixed vapour streams was 50% RH. To ensure a particle-free atmosphere, both gas streams were double-filtered, first with a Fluoropore Teflon membrane filter (37-mm diameter, 1.0- $\mu$ m pore size, FALP 03700, Millipore Corp., Bedford, MA) and followed by a laminated glass-fibre filter (part no. 6004300, Gelman Sciences, Ann Arbor, MI). Steady-state nicotine concentrations in the gas stream were achieved by allowing the system to equilibrate overnight ( $\geq$  18 hrs) prior to all sample collections.

The lack of particles in the gas stream being sampled was verified with a condensation nucleus counter (CNC, model no. 3020, TSI Inc., St. Paul, MN).

### Nicotine Collection

Sampling systems used for trapping nicotine consisted of an XAD-4 sorbent tube (226-30-11-04, SKC Inc., Eighty-Four, PA) connected downstream from either a borosilicate glass-fibre filter (T60A20, Pallflex Co., Putnam, CT) or a Teflon membrane filter (Fluoropore FALP 03700). In both cases, a bisulfate-treated glass-fibre filter (Pallflex TX40HI20WW) was positioned downstream from the XAD-4 sorbent tube to ensure that all nicotine was collected (12). In all cases, connecting tubing was kept to an absolute minimum. Flow through each sample train was maintained at 2.2 L min<sup>-1</sup> using an electronic mass flow controller (Teledyne Hastings-Raydist, Hampton, VA). A second mass flow controller was adjusted to dilute the nicotine vapour from the gas standards generator to a level comparable to that employed by Neurath *et al.* (9); the target concentration was 1500  $\mu$ g m<sup>-3</sup>. Likewise, the untreated glass-fibre filter (Pallflex T60A20) and flow rate through the sample train (2.2 L min<sup>-1</sup>) are the same as used by Neurath *et al.* (9). The entire experimental set-up is represented schematically in Figure 1.

Five replicates were obtained with each sampling system at each of 1-, 2-, 3-, 5-, and 10-min collection times. All samples were extracted and analyzed within 48 hrs of sample collection.

### Analytical Methods

Nicotine collected on XAD-4, untreated glass-fibre filters (Pallflex), and Teflon filters (Fluoropore) was extracted in triethylamine-modified ethyl acetate followed by gas chromatography with *N*-thermionic detection using quinoline as internal standard (13-16).

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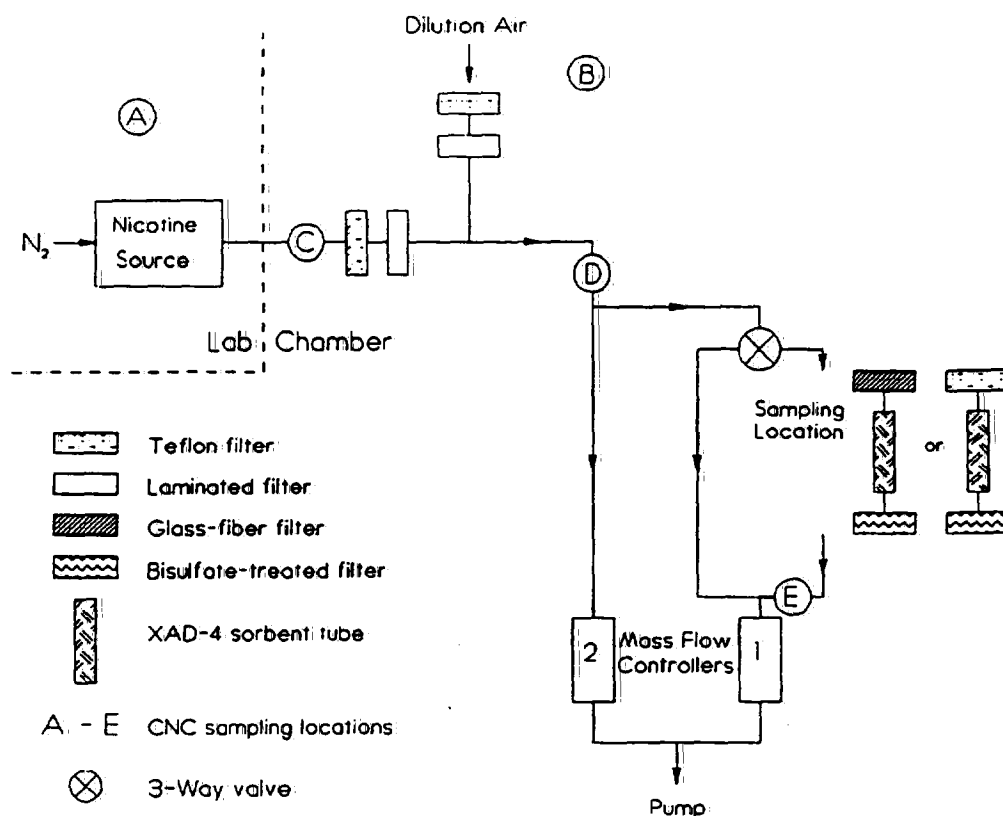


Figure 1. Schematic diagram of experimental set-up. 3-Way valve is used to direct nicotine vapour either through sample train or to bypass.

Nicotine trapped on bisulfate-treated glass-fibre filters was extracted in ethanol-modified sodium hydroxide with back extraction into ammoniated heptane (12). Gas chromatographic conditions were the same as for the XAD procedure except that *N*-ethylnornicotine was used as internal standard.

In preliminary experiments, it was confirmed that nicotine recovery from the

untreated glass-fibre filter was equivalent when using either the direct ethyl acetate extraction or the more cumbersome sodium hydroxide/heptane partitioning.

## RESULTS AND DISCUSSION

Particle concentrations at each sampling point denoted in Figure 1 are listed in Table 1.

Table 1. Particle concentrations at sampling points illustrated in Figure 1 as measured by a condensation nucleus counter (CNC).

| Sample Location Descriptor        | Sampling Position<br>Noted in Figure 1 | CNC Response<br>(particles $\text{cm}^{-3}$ )* |
|-----------------------------------|--|--|
| Laboratory air                    | A                                      | $7.3 \times 10^3$                              |
| Chamber air                       | B                                      |  |
| experiment start                  |  | $4.2 \times 10^1$                              |
| experiment end                    |  | $1.3 \times 10^3$                              |
| Before filters                    | C                                      | $0.03 \times 10^0$                             |
| After filters/before sample train | D                                      | $0.00 \times 10^0$                             |
| After sample train                | E                                      | $0.00 \times 10^0$                             |

\*Data presentation reflects reading and range values as determined by the CNC.

Table 2. Vapour-phase nicotine retained on filter collection media as a function of sampling duration.

| Sampling Duration<br>(min) | Pallflex (glass-fibre) filter<br>( $\pm$ SE, n=5) |                | Fluoropore (Teflon) filter<br>( $\pm$ SE, n=5) |               |
|----------------------------|---|----------------|--|---------------|
|                            | $\mu\text{g. filter}^{-1}$                        | % of total     | $\mu\text{g. filter}^{-1}$                     | % of total    |
| 1                          | $3.46 \pm 0.02$                                   | $97.3 \pm 0.2$ | $0.14 \pm 0.01$                                | $4.9 \pm 0.3$ |
| 2                          | $5.15 \pm 0.20$                                   | $75.3 \pm 2.0$ | $0.16 \pm 0.01$                                | $2.4 \pm 0.2$ |
| 3                          | $6.09 \pm 0.17$                                   | $62.1 \pm 1.6$ | $0.17 \pm 0.01$                                | $1.8 \pm 0.1$ |
| 5                          | $6.20 \pm 0.34$                                   | $38.2 \pm 1.6$ | $0.27 \pm 0.03$                                | $1.5 \pm 0.2$ |
| 10                         | $6.95 \pm 0.36$                                   | $20.3 \pm 0.5$ | $0.28 \pm 0.06$                                | $0.8 \pm 0.1$ |

The complete absence of any measurable particle concentration directly upstream from the sample collection assembly verifies the presence of only vapour-phase nicotine. The average concentration ( $\pm$  SE, n=50) of nicotine vapour being sampled was  $1513 \mu\text{g m}^{-3}$  ( $\pm 18$ ).

Results of nicotine determination on the two filter collection media are presented in Table 2. As can be seen, the untreated glass-fibre filter has a substantial capacity for adsorbing nicotine. Shown in Figure 2 is a plot of nicotine mass

adsorbed on the untreated glass-fibre filter (Pallflex) as a function of sample duration showing an adsorptive capacity approaching  $7 \mu\text{g}$  under the atmospheric conditions used. Although there appears to be an increasing trend still present between five and 10 min, these two values are not statistically different. Also shown in Figure 2 is the minimal quantity of vapour-phase nicotine trapped by Teflon filters under identical conditions.

The filter/XAD-4 combinations trapped

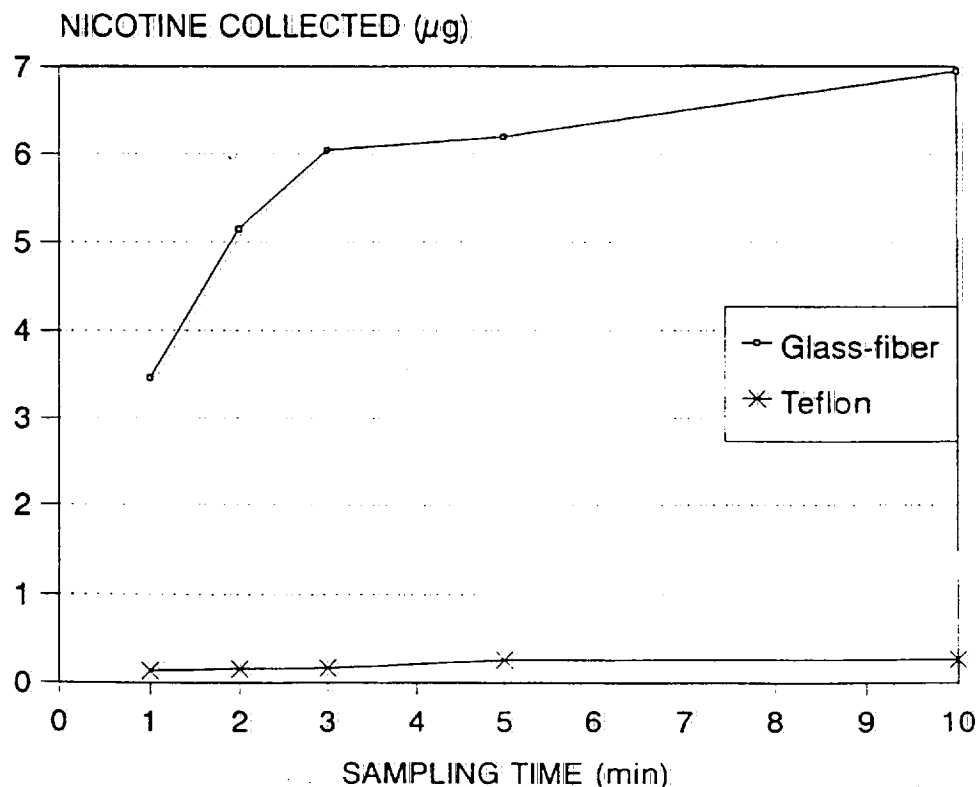


Figure 2. Vapour-phase nicotine retained on borosilicate glass-fibre (Pallflex T60A20) and Teflon (Fluoropore) filters as a function of sampling duration.

>99% of the total vapour-phase nicotine. The average ( $\pm$  SE,  $n=50$ ) nicotine breaking through onto the bisulfate-treated filter was 0.8% ( $\pm$  0.2).

Expressing the quantities of nicotine retained on the first filter as a percentage of the total amount collected by each sample train (Figure 3) shows that with only 1-min sampling, nearly all of the vapour-phase nicotine (>97%) is trapped on the glass-fibre filter. In contrast, nicotine collected on the Teflon filter ranges from ca. 5 to 1% of the total at collection times ranging from 1 to 10 min.

The phenomenon illustrated by these data is the same as that observed by Neurath *et al.* (8,9) and Esquier and H  e (10). However, to attribute these results to the presence and collection of particulate-phase nicotine, two assumptions must be valid. First, the glass-fibre filter used must trap only particulate-phase nicotine and allow vapour-phase nicotine to pass unhindered. Second, any collected nicotine associated with the particulate matter must be stable and will not be evaporated from the particles (and thus lost to the backup sorbent resin) under the influence of the continuous air stream being sampled.

The data presented here demonstrate that the first assumption is not valid for glass-fibre

filters. Assuming that all nicotine retained by a glass-fibre filter derives from particulate-phase nicotine will result in gross overestimation of the nicotine associated with that phase. The degree of overestimation is most pronounced with very short sampling times of only a few minutes.

This phenomenon had already been demonstrated in the literature for Cambridge (glass-fibre) filters (2). Other data in the literature show ca. 1  $\mu$ g of nicotine adsorbed completely from solution onto the inside surfaces of borosilicate glass vials (14). It appears reasonable, therefore, that a borosilicate glass-fibre filter with several orders of magnitude more surface area than a glass vial could adsorb at least one order of magnitude more nicotine from air. Our results indicate that the glass-fibre filters used here and elsewhere (8,9) are an efficient collection medium for vapour-phase nicotine at sampling times of a few minutes or less. We have not attempted to show what dependence the nicotine adsorption on glass-fibre filters may have on sampling time, air flow rate, temperature, RH, or nicotine concentration.

Likewise, there are data in the literature

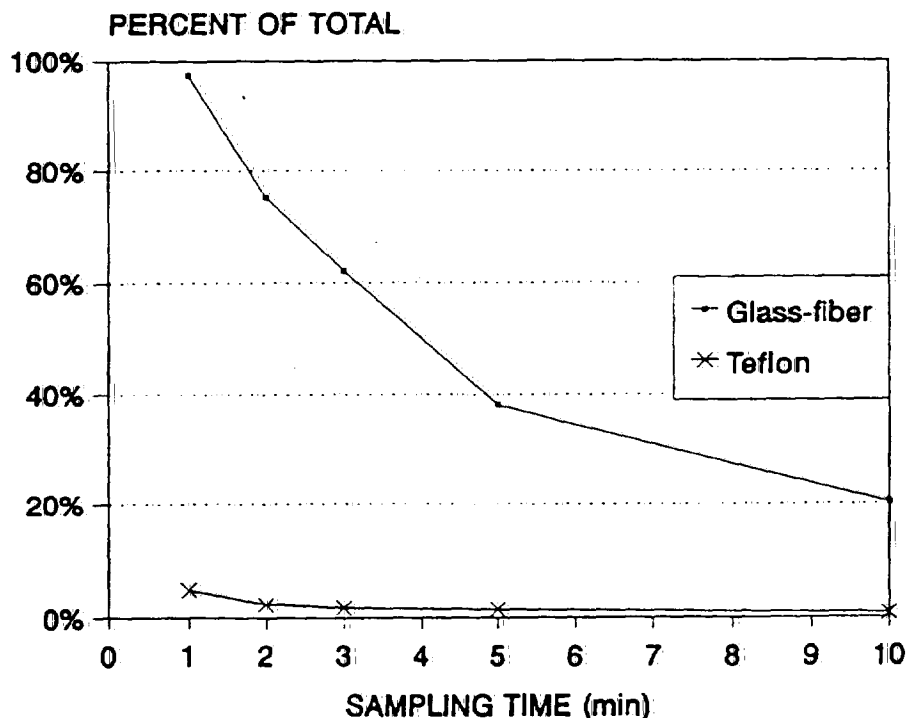


Figure 3. Percentage of total vapour-phase nicotine trapped by borosilicate glass-fibre (Pallflex T60A20) and Teflon (Fluoropore) filters as a function of sampling duration.

which negate the second assumption outlined above. In an intercomparison study of sampling techniques for nicotine (17), untreated glass-fibre filters used to collect particulate-phase nicotine passing through denuders yielded results which were biased low compared to acid-treated filters used after denuders. Esquier and Hée (10) also correctly identified the problem of nicotine evaporation from an untreated filter during sampling.

Any nicotine truly present in the aerosol particulate phase would be trapped initially by glass-fibre filters. However, this minute quantity will be totally obscured by simultaneous collection of nicotine vapour. Combined with the almost certain loss of some true particulate-phase nicotine due to evaporation and elution from the filters, the data obtained from use of such filter systems are completely

uninterpretable with respect to the vapour-particulate phase dynamics of ETS nicotine.

#### CONCLUSION

Use of combined filter/sorbent sampling systems for studying the distribution and dynamics of nicotine between aerosol phases is inappropriate. Borosilicate glass-fibre filters collect virtually all nicotine (vapour- and particulate-phase) at relatively short sampling intervals (1-2 min). Using such a system, only that amount of total nicotine which exceeds the adsorptive capacity of the filter will break through and be collected by the sorbent medium. Attributing ETS particulate-phase nicotine to the quantity collected on the glass-fibre filter leads to erroneous conclusions.

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